

## Crystal Structure of *mer*-Tris-(*N*-benzylsalicylaldiminato)manganese(III)

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The crystal structure of the title compound has been determined by the heavy-atom method from X-ray diffractometer data and refined by least-squares to  $R = 0.05$  (2991 reflections). Crystals are triclinic, space group  $P\bar{1}$ ,  $a = 11.054(2)$ ,  $b = 16.462(3)$ ,  $c = 9.801(2)$  Å,  $\alpha = 104.91(1)$ ,  $\beta = 93.20(2)$ ,  $\gamma = 94.02(2)^\circ$ ,  $Z = 2$ .

The three ligands are bidentate, co-ordinating through the oxygen and nitrogen atoms in the *mer*-conformation, i.e. *trans*-isomer. The manganese environment displays a pseudo-tetragonal distortion, the axial atoms being nitrogen [ $Mn-N$  2.251(5) and 2.271(5) Å]. The equatorial atoms are at distances:  $Mn-O$  1.882(3), 1.896(3), and 1.917(4), and  $Mn-N$  2.082(5) Å.

As part of our study<sup>1</sup> on distortions in octahedral manganese(III) complexes we report here the crystal structure of tris-(*N*-benzylsalicylaldiminato)manganese(III),<sup>2</sup> a compound containing an unsymmetrical bidentate ligand. This is the first reported crystal structure of a tris-(*N*-substituted salicylaldimine) derivative. The n.m.r. studies of Holm and co-workers<sup>3,4</sup> have shown that related cobalt(III) and vanadium(III) complexes exist in solution exclusively as the *trans*- or *mer*-isomer; they attribute this to steric crowding between adjacent substituted-nitrogen atoms. Our work supports these conclusions for manganese(III), at least in the crystalline state.

### EXPERIMENTAL

Material used was prepared as described previously<sup>2</sup> and recrystallized from benzene. A single prismatic crystal 0.26 × 0.16 × 0.19 mm was used throughout the data collection.

A complete independent set (3458 reflections) of X-ray data was collected in the range  $20 < 100^\circ$  (nickel-filtered  $Cu-K_\alpha$  radiation,  $\lambda = 1.5418$  Å)<sup>5</sup> using a conventional 20/0 scan on a Syntex P1 four-circle diffractometer. 2991 Reflections having  $I > \sigma(I)$  were used with unit weights in the structure determination and refinement. Unit-cell calibration was effected by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture. Computation, including absorption correction, was carried out by use of a local adaptation of the X-Ray '72 system.<sup>6</sup>

*Crystal Data.*— $C_{42}H_{36}N_3O_3Mn$ ,  $M = 685.71$ , Triclinic,  $a = 11.054(2)$ ,  $b = 16.462(3)$ ,  $c = 9.801(2)$  Å,  $\alpha = 104.91(1)$ ,  $\beta = 93.20(2)$ ,  $\gamma = 94.02(2)^\circ$ ,  $U = 1714.1(6)$  Å<sup>3</sup>,  $D_m$  (floatation) 1.32,  $Z = 2$ ,  $D_c$  1.33 g cm<sup>-3</sup>. Space group  $P\bar{1}$  ( $C_i^1$ , No. 2).<sup>7</sup>  $\mu(Cu-K_\alpha) = 36.5$  cm<sup>-1</sup>. Scattering factors for the neutral atoms were taken from ref. 8, that for manganese being corrected for anomalous dispersion ( $\Delta f'$ ,  $\Delta f''$ ).<sup>9</sup> No extinction correction was applied. The structure was solved by the heavy-atom method, and refined by 9 × 9 block-diagonal least-squares for the non-hydrogen atoms incorporating anisotropic thermal motion according to the

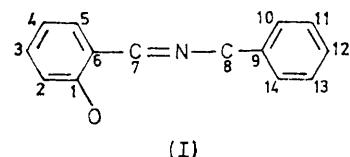
\* Structure factors are listed in Supplementary Publication No. SUP 21031 (16 pp., 1 microfiche); details of hydrogen atom parameters are also listed. For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

<sup>1</sup> P. C. Healy and A. H. White, *J.C.S. Dalton*, 1972, 1885.

<sup>2</sup> A. van de Bergen, K. S. Murray, M. J. O'Connor, and B. O. West, *Austral. J. Chem.*, 1969, **22**, 1699.

<sup>3</sup> A. Chakravorty and R. H. Holm, *Inorg. Chem.*, 1964, **3**, 1521.

form:  $\exp[-2\pi^2(U_{11}h^2a^*{}^2 + U_{22}k^2b^*{}^2 + U_{33}l^2c^*{}^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ . In the last few cycles, a full-matrix refinement of the manganese and its environment was 'faked' by refining the parameters of the  $MnN_3O_3$  molecular core as a single block; hydrogen atom positions were calculated and refined positionally, thermal parameters being fixed isotropically at  $U = 0.09$  Å<sup>2</sup>. In the final cycle no parameter shift exceeded  $0.15\sigma$ ;  $R$  was 0.052, and  $R' = 0.056 \{R' [\Sigma(|F_o| - |F_c|)^2 / \Sigma |F_o|^2]\}^{1/2}$ . A final difference map showed no significant features.† The numbering of the carbon atoms (and associated hydrogens) within each ligand is shown in (I). Results are shown in Tables 1–3.



(I)

### DISCUSSION

As expected, the structure is comprised of discrete molecules (Figure); within each molecule, the three *N*-benzylsalicylaldiminato-groups act as bidentate ligands about the central manganese atom, co-ordinating through the nitrogen and oxygen atoms. The  $MnO_3N_3$  molecular core has the *mer*- or *trans*-configuration; this is in accord with the findings of a number of synthetic,<sup>10</sup> spectroscopic,<sup>10</sup> and n.m.r.<sup>3,4,10</sup> studies on these and other complexes of the general class,  $M(N$ -substituted salicylaldiminate)<sub>3</sub> and has been attributed to steric crowding between the three substituted nitrogen atoms being too dense to allow them to occupy the same triangular octahedron face.

As in other 'octahedral' manganese(III) complexes whose structures have been studied, a pronounced pseudo-tetragonal distortion from octahedral symmetry is observed, normally ascribed to loss of degeneracy by

<sup>4</sup> F. Rorscheid, R. E. Grust, and R. H. Holm, *J. Amer. Chem. Soc.*, 1967, **89**, 6472.

<sup>5</sup> 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1969, p. 59.

<sup>6</sup> 'X-Ray' system of programs, version of June 1972, Technical Report TR 192 of the Computer Science Centre, University of Maryland, U.S.A.

<sup>7</sup> Ref. 5, vol. 1, 2nd edn., 1965, p. 75.

<sup>8</sup> Ref. 5, p. 202.

<sup>9</sup> Ref. 5, p. 215.

<sup>10</sup> B. O. West, *J. Chem. Soc.*, 1960, 4944.

TABLE 1

Atomic fractional cell ( $x, y, z \times 10^4$ ) and anisotropic thermal parameters ( $10^3 U_{ij} \text{ \AA}^2$ ), with least-squares estimated standard deviations in parentheses, for non-hydrogen atoms

Atom	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Mn*	21966(8)	22574(5)	17326(9)	24.0(6)	42.2(6)	37.0(6)	7.6(4)	-1.3(4)	5.4(4)
(i) Ligand (a)									
O(a)	2836(3)	1463(2)	0270(3)	49(2)	46(2)	34(2)	16(2)	0(2)	8(2)
N(a)	1277(4)	2705(3)	0201(4)	46(3)	40(3)	45(3)	9(2)	-8(2)	4(2)
C(1a)	2389(5)	1121(3)	-1049(5)	43(3)	40(3)	30(3)	1(3)	2(3)	6(3)
C(2a)	2843(6)	0370(3)	-1797(6)	60(4)	38(3)	50(4)	13(3)	9(3)	7(3)
C(3a)	2455(6)	0017(4)	-3192(6)	69(5)	51(4)	49(4)	8(3)	13(3)	2(3)
C(4a)	1621(6)	0377(4)	-3902(6)	86(5)	58(4)	30(3)	5(4)	-3(3)	-1(3)
C(5a)	1171(6)	1109(4)	-3193(6)	66(4)	56(4)	35(3)	13(3)	-1(3)	3(3)
C(6a)	1543(5)	1492(3)	-1755(5)	55(4)	44(4)	34(3)	16(3)	1(3)	10(3)
C(7a)	1115(5)	2296(4)	-1109(6)	53(4)	49(4)	42(3)	11(3)	-11(3)	9(3)
C(8a)	0848(7)	3574(4)	0636(7)	99(6)	47(4)	71(5)	35(4)	-27(4)	-7(3)
C(9a)	-0241(5)	3726(3)	-0222(6)	53(4)	38(3)	40(3)	16(3)	-5(3)	4(3)
C(10a)	-1401(7)	3530(4)	0116(7)	95(6)	74(5)	72(5)	19(4)	30(4)	39(4)
C(11a)	-2411(6)	3701(5)	-0660(9)	43(4)	105(6)	115(7)	11(4)	18(4)	27(5)
C(12a)	-2243(6)	4051(4)	-1734(7)	69(5)	72(5)	69(5)	25(4)	-12(4)	11(4)
C(13a)	-1141(7)	4244(4)	-2083(6)	92(5)	53(4)	48(4)	25(4)	2(4)	10(3)
C(14a)	-0135(6)	4081(4)	-1331(6)	53(4)	46(4)	57(4)	10(3)	10(3)	8(3)
(ii) Ligand (b)									
O(b)	2990(3)	1741(2)	3040(4)	54(3)	46(2)	35(2)	7(2)	-9(2)	7(2)
N(b)	0573(4)	1332(3)	1733(4)	39(3)	47(3)	38(3)	9(2)	-2(2)	0(2)
C(1b)	2972(5)	0915(4)	2867(5)	55(4)	49(4)	28(3)	9(3)	9(3)	11(3)
C(2b)	4025(5)	0583(4)	3326(6)	52(4)	58(4)	47(4)	10(3)	0(3)	17(3)
C(3b)	4039(6)	-0261(4)	3219(7)	53(4)	71(5)	66(4)	25(4)	7(3)	23(4)
C(4b)	3028(6)	-0822(4)	2700(7)	69(5)	58(4)	61(4)	17(4)	9(4)	17(3)
C(5b)	1992(6)	-0509(4)	2254(6)	53(4)	58(4)	47(4)	2(3)	5(3)	12(3)
C(6b)	1938(5)	0351(3)	2328(5)	52(4)	39(3)	32(3)	3(3)	4(3)	7(3)
C(7b)	0770(5)	0596(4)	1871(5)	45(4)	53(4)	33(3)	6(3)	3(3)	0(3)
C(8b)	0697(5)	1435(4)	1343(6)	41(4)	59(4)	52(4)	2(3)	-6(3)	7(3)
C(9b)	-1427(5)	1833(4)	2586(6)	40(3)	47(4)	51(4)	4(3)	5(3)	12(3)
C(10b)	-2638(6)	1926(4)	2321(7)	50(4)	63(4)	68(4)	10(3)	1(3)	28(3)
C(11b)	-3376(6)	2219(4)	3425(7)	46(4)	58(4)	93(5)	11(3)	11(4)	32(4)
C(12b)	-2863(6)	2422(4)	4806(7)	69(5)	53(4)	75(5)	12(4)	20(4)	11(4)
C(13b)	-1652(6)	2352(4)	5065(6)	66(5)	70(5)	54(4)	6(4)	6(3)	6(3)
C(14b)	-0929(6)	2049(4)	3976(6)	53(4)	62(4)	50(4)	1(3)	4(3)	6(3)
(iii) Ligand (c)									
O(c)	1572(3)	3059(2)	3221(4)	46(2)	43(2)	43(2)	0(2)	5(2)	-3(2)
N(c)	3751(4)	3243(3)	1879(4)	38(3)	56(3)	31(3)	5(2)	-3(2)	12(2)
C(1c)	1937(6)	3817(4)	3999(7)	45(5)	41(5)	30(4)	6(4)	-5(3)	10(3)
C(2c)	1195(5)	4197(4)	5060(6)	57(4)	44(4)	43(4)	8(3)	0(3)	6(3)
C(3c)	1517(6)	5003(4)	5907(6)	66(5)	56(4)	55(4)	14(3)	-2(3)	11(3)
C(4c)	2551(6)	5457(4)	5757(6)	86(5)	37(4)	51(4)	12(3)	-13(3)	4(3)
C(5c)	3306(6)	5107(4)	4735(6)	56(4)	47(4)	47(4)	1(3)	-11(3)	11(3)
C(6c)	3016(5)	4284(3)	3841(5)	49(4)	40(3)	31(3)	2(2)	-7(3)	8(3)
C(7c)	3872(5)	3964(4)	2808(6)	48(4)	65(4)	36(3)	-5(3)	-9(3)	14(3)
C(8c)	4726(5)	3047(4)	0930(6)	38(4)	81(5)	45(4)	11(3)	2(3)	18(3)
C(9c)	4366(5)	3104(4)	-0556(6)	33(3)	67(4)	48(4)	8(3)	6(3)	17(3)
C(10c)	4459(6)	2407(4)	-1690(6)	52(4)	82(5)	49(4)	3(4)	2(3)	23(3)
C(11c)	4153(7)	2429(5)	-3048(7)	70(5)	112(7)	62(5)	3(5)	3(4)	26(4)
C(12c)	3768(8)	3115(7)	-3296(8)	88(6)	184(10)	66(5)	24(6)	4(4)	60(6)
C(13c)	3665(8)	3836(6)	-2254(10)	90(6)	115(7)	132(7)	40(5)	18(5)	81(6)
C(14c)	3977(7)	3825(5)	-0816(7)	77(5)	82(5)	73(5)	27(4)	14(4)	32(4)

\* Mn co-ordinates  $\times 10^5$ .

TABLE 2

Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ), with least-squares estimated standard deviation in parentheses

## (a) The Mn environment

Mn—O(a)	1.882(3)	Mn—N(a)	2.082(5)
Mn—O(b)	1.917(4)	Mn—N(b)	2.271(5)
Mn—O(c)	1.896(3)	Mn—N(c)	2.251(5)
O(a)—Mn—O(b)	87.6(2)	O(a)—Mn—N(c)	93.5(2)
O(a)—Mn—O(c)	179.2(2)	O(b)—Mn—N(a)	174.6(2)
O(b)—Mn—O(c)	91.9(2)	O(b)—Mn—N(b)	85.5(2)
N(a)—Mn—N(b)	90.6(2)	O(b)—Mn—N(c)	94.2(2)
N(a)—Mn—N(c)	89.9(2)	O(c)—Mn—N(a)	91.9(2)
N(b)—Mn—N(c)	175.6(2)	O(c)—Mn—N(b)	89.5(2)
O(a)—Mn—N(a)	88.8(2)	O(c)—Mn—N(c)	86.1(2)
O(a)—Mn—N(b)	90.9(2)		

## (b) The ligands

	Ligand	(a)	(b)	(c)
O—C(1)		1.322(5)	1.325(7)	1.306(7)
C(1)—C(2)		1.407(7)	1.419(9)	1.406(9)
C(2)—C(3)		1.372(8)	1.367(9)	1.382(8)
C(3)—C(4)		1.379(9)	1.382(9)	1.357(9)
C(4)—C(5)		1.369(9)	1.382(10)	1.378(9)
C(5)—C(6)		1.412(7)	1.405(8)	1.415(7)
C(6)—C(1)		1.397(8)	1.407(7)	1.411(9)
C(6)—C(7)		1.437(8)	1.460(8)	1.449(8)
C(7)—N		1.283(6)	1.285(9)	1.290(7)
N—C(8)		1.502(8)	1.468(7)	1.462(7)
C(8)—C(9)		1.502(9)	1.528(9)	1.516(9)
C(9)—C(10)		1.379(9)	1.376(9)	1.391(8)
C(10)—C(11)		1.401(10)	1.398(9)	1.365(10)
C(11)—C(12)		1.339(12)	1.386(9)	1.309(14)
C(12)—C(13)		1.317(10)	1.367(9)	1.368(13)
C(13)—C(14)		1.385(10)	1.380(9)	1.437(12)
C(14)—C(9)		1.367(9)	1.387(8)	1.369(11)
Mn—O—C(1)		129.8(3)	124.1(3)	135.7(4)
O—C(1)—C(2)		118.0(5)	118.5(5)	117.6(6)
C(1)—C(2)—C(3)		120.0(6)	120.9(5)	120.7(6)
C(2)—C(3)—C(4)		121.9(6)	121.8(6)	121.8(6)
C(3)—C(4)—C(5)		119.0(5)	118.0(6)	119.4(5)
C(4)—C(5)—C(6)		121.0(6)	122.2(5)	120.9(6)
C(5)—C(6)—C(1)		119.5(5)	119.1(5)	119.5(5)
C(6)—C(1)—O		123.2(4)	123.5(5)	124.7(5)
C(6)—C(1)—C(2)		118.7(4)	117.9(6)	117.7(5)
C(1)—C(6)—C(7)		122.2(4)	124.7(5)	123.4(5)
C(5)—C(6)—C(7)		118.0(5)	118.2(5)	117.0(5)
C(6)—C(7)—N		126.9(6)	125.3(5)	126.1(5)
C(7)—N—Mn		123.4(4)	118.5(4)	123.8(4)
C(7)—N—C(8)		118.3(5)	114.9(10)	117.1(5)
Mn—N—C(8)		118.2(3)	125.7(3)	118.9(3)
C(8)—C(9)—C(14)		122.3(6)	122.0(6)	122.0(5)
C(9)—C(10)—C(11)		120.0(7)	121.2(6)	121.0(7)
C(10)—C(11)—C(12)		119.6(7)	118.6(6)	119.8(6)
C(11)—C(12)—C(13)		121.6(7)	121.0(6)	123.3(8)
C(12)—C(13)—C(14)		119.6(7)	121.3(6)	117.7(9)
C(13)—C(14)—C(9)		121.9(6)	119.6(6)	118.9(6)
C(14)—C(9)—C(10)		117.2(6)	119.2(6)	119.1(6)

(c) Intermolecular ( $H \cdots H < 2.7$ , other  $< 3.0 \text{ \AA}$ )

C(8c) $\cdots$ H(11a <sup>I</sup> )	2.75(7)	H(8c <sup>2</sup> ) $\cdots$ H(11b <sup>I</sup> )	2.62(9)
C(2b) $\cdots$ H(11c <sup>II</sup> )	2.94(6)	H(2c) $\cdots$ H(13a <sup>II</sup> )	2.54(9)
C(5b) $\cdots$ H(4a <sup>II</sup> )	2.90(6)	H(4a) $\cdots$ H(6b <sup>III</sup> )	2.95(7)
H(11c) $\cdots$ H(2b <sup>III</sup> )	2.56(8)	H(13a) $\cdots$ H(3c <sup>III</sup> )	2.43(9)
H(11a) $\cdots$ C(9c <sup>IV</sup> )	2.59(6)	H(11a) $\cdots$ C(10c <sup>IV</sup> )	2.95(6)
C(11b) $\cdots$ H(2b <sup>IV</sup> )	2.79(7)	H(11a) $\cdots$ H(8c <sup>IV</sup> )	2.17(9)
H(3b) $\cdots$ H(11c <sup>V</sup> )	2.66(10)	C(5c) $\cdots$ H(12a <sup>VI</sup> )	2.95(7)
C(10b) $\cdots$ H(3a <sup>VI</sup> )	2.97(7)	C(11b) $\cdots$ H(3a <sup>VI</sup> )	2.98(6)
C(2a) $\cdots$ H(8b <sup>VI</sup> )	2.99(7)	C(5a) $\cdots$ H(5b <sup>VII</sup> )	2.98(7)
H(4c) $\cdots$ C(11b <sup>VIII</sup> )	2.96(6)		

Roman numeral superscripts refer to the following transformations of the asymmetric unit ( $x, y, z$ ):

I  $1 + x, y, z$   
 II  $x, y, z - 1$   
 V  $1 - x, \bar{y}, z$   
 VII  $\bar{x}, \bar{y}, \bar{z}$

II  $x, y, 1 + z$   
 IV  $1 - x, y, z$   
 VI  $\bar{x}, 1 - y, \bar{z}$   
 VIII  $\bar{x}, 1 - y, 1 - z$

the  ${}^5E_g$  ground-state; this normally occurs by means of the 'four short, two long' configuration. In the

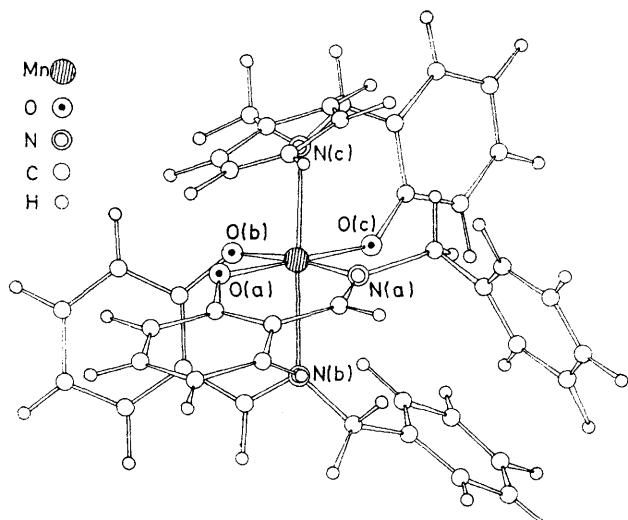
TABLE 3

Equations of best least-squares planes in the form  $pX + qY + rZ = s$ , with deviations ( $\text{\AA}$ ) of relevant atoms in square brackets;  $\sigma$  is the standard deviation ( $\text{\AA}$ ) of atoms defining the plane.  $X, Y, Z$  are orthogonal ( $\text{\AA}$ ) axes, derived from the triclinic cell by the transformation:  $X$  parallel to  $a$ ;  $Z$  lies in the  $abc$  plane

	$p$	$q$	$r$	$s$	$\sigma/\text{\AA}$
<i>(a)</i> Planes through the metal atom					
Plane (i): O(a), N(b), O(c), N(c)	-0.4914	0.3539	-0.7958	-0.3370	0.00
[O(a), N(b), O(c), N(c), Mn, 0.00]					
Plane (ii): O(a), N(a), O(b), O(c)	0.7577	0.6389	-0.1349	3.7271	0.04
[O(a), O(c) 0.04; O(b), N(a) -0.04; Mn 0.03]					
Plane (iii): N(a), O(b), N(b), N(c)	-0.4802	0.6513	0.5876	1.7718	0.08
[N(a), O(b) -0.08; N(b), N(c) 0.08; Mn -0.01]					
<i>(b)</i> Planes through the ligands					
Plane (iv): O(a), N(a), C(1a) — (7a)	0.7309	0.5208	-0.4411	3.4946	0.03
[O(a) 0.03, N(a) -0.04, C(1a) -0.03, C(2a) -0.01, C(3a) 0.01, C(4a) 0.01, C(5a) -0.01, C(6a) -0.03, C(7a) 0.07, Mn -0.44, C(8a) 0.22]					
Plane (v): C(9a) — (14a)	-0.0863	0.9096	0.4065	4.6864	0.00
[C(9a) — (14a) 0.00, C(8a) 0.05]					
Plane (vi): O(b), N(b), C(1b) — (7b)	-0.3878	0.1483	0.9097	1.2511	0.04
[O(b) 0.04, N(b) -0.07, C(1b) -0.01, C(2b) -0.01, C(3b) -0.02, C(4b) 0.00, C(5b) 0.01, C(6b) 0.00, C(7b) 0.06, Mn -0.87, C(8b) 0.11]					
Plane (vii): C(9b) — (14b)	0.1623	0.9374	-0.3082	1.8795	0.01
[C(9b) -0.01, C(10b) 0.01, C(11b) 0.00, C(12b) -0.01, C(13b) 0.01, C(14b) -0.00, C(8b) -0.13]					
Plane (viii): O(c), N(c), C(1c) — (7c)	-0.4881	0.3842	-0.7837	-0.1737	0.01
[O(c) 0.01, N(c) 0.01, C(1c) -0.01, C(2c) -0.01, C(3c) 0.00, C(4c) 0.01, C(5c) 0.01, C(6c) 0.00, C(7c) -0.02, Mn -0.03, C(8c) 0.00]					
Plane (ix): C(9c) — (14c)	0.9295	0.3249	-0.1746	6.1135	0.00
[C(9c) — (14c) 0.00, C(8c) 0.01]					

present case, the possibility of distortion along either the O—Mn—O, O—Mn—N, or N—Mn—N axes arises; it is found

experimentally that in fact the donors along the elongated axis are the pair of nitrogen atoms, [Mn–N(b,c) 2.271, 2.251(5) Å], the remaining three oxygen atoms



A diagram of the molecule projected down  $c$

and the nitrogen atom of ligand (a) lying in the equatorial plane [Mn–O(a,b,c) 1.882, 1.917, and 1.896(3); Mn–N(a), 2.082(5) Å].

Within the equatorial ligand (a), the O–Mn–N angle is 88.8(2) $^\circ$ , appreciably greater than the corresponding angles associated with ligands (b) and (c) [85.5(2) and 86.1(2) $^\circ$ ], the difference presumably being indicative of the greater strain within the ligand in spanning the greater axial-equatorial chelate distance. Although pronounced irregularities are found in the Mn–O–C(1) angles within each ligands [ranging from 124.1 to 135.7(4) $^\circ$ ] there appears to be no systematic basis for this variation and it is not reflected in e.g. the O–C(1) bond lengths. A similar variation occurs in the Mn–N–C(8) angles. These variations appear to be symptomatic of a

general molecular flexibility. The deviations of the manganese atom from the generally good ligand plane (0.44, 0.87, and 0.03 Å) suggest a lack of any strong metal-ligand  $\pi$  bonding. Comparison of the manganese–oxygen and –nitrogen distances with those observed in other manganese(III) complexes with oxygen- and nitrogen-containing ligands and relatively unstrained ligand geometry reveals a wide diversity (Table 4). However,

TABLE 4

Axial and equatorial bond lengths ( $r_a$  and  $r_e$  Å) reported in six-co-ordinate manganese(III) complexes with oxygen- and nitrogen-containing ligands, showing tetrahedral distortion

Complex *	$r_a$ (O)	$r_e$ (O)	$r_a$ (N)	$r_e$ (N)
(A)		1.88–1.90(2)	2.25–2.27(2)	2.08(2)
(B)	2.134(5)	1.959(5)	2.153(5)	2.020(5)
(C)	2.227(4)	1.90(1)	2.534(4)	1.967(4)
(D)	2.12	1.95		
(E)	2.20	1.89		

\* (A) *mer*-Tris-(*N*-benzylsalicylaldiminato)manganese(III), (this work); (B) acetylacetonebis-(*N*-phenylaminotropone-iminato)manganese(III) (M. Bartlett and G. Palenik, *Chem. Comm.*, 1970, 416); (C) di- $\mu$ -methoxy-bis(salicylaldhyde-anthranylhydrazone)dimanganese(III) (A. Mangia, M. Nardelli, C. Pelizzi, and G. Palizzi, *J.C.S. Dalton*, 1973, 1141); (D) tris(tropolonato)manganese(III) (J. P. Fackler, A. Aydec, and J. Costamagna, *Proc. XIV I.C.C.C.*, 1972, 589); (E) *catena*-acetato[bis(ethylenesalicylidene)caldimato]manganese(III) (J. E. Davies, B. M. Gatehouse, and K. S. Murray, *J.C.S. Dalton*, 1973, 2523).

as these structures are diverse in other respects, e.g. not all are mononuclear, more data appears to be necessary for any useful speculation as to the nature and origin of these large variations.

The ligand geometries are unremarkable. Variations within the benzene ring geometries are particularly evident in the peripheries of the phenyl substituent and are probably a consequence of their higher thermal motion, since no correction was applied.